

Attachment of Amino Groups to Polymer Surfaces by Radiofrequency Plasmas

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Synopsis

Low temperature gaseous plasmas of ammonia or nitrogen-hydrogen mixtures contain —NH_2 groups, or precursors thereof, formed in the plasma, which experimental evidence strongly suggests, can add to various polymer surfaces. The plasmas were established in the 0.3–1.5 torr range by radiofrequency (13.56 MHz) electrodeless excitation at powers ranging from 50 to 500 W. Samples of polypropylene, poly(vinyl chloride), polytetrafluoroethylene, polycarbonate, polyurethane, and poly(methyl methacrylate) were investigated. All these polymers added amino groups to varying degrees of amino site densities depending on the choice of plasma parameters and the reactivity of the polymer itself. In every instance the polymer was rendered more wettable, although no quantitative wettability measurements were made. Following the plasma treatment, degrees of amino attachment to the polymer were followed radio-metrically and reported in terms of "heparin thicknesses" resulting from ionic heparin $\text{—}^{35}\text{S}$ attachment to quaternary sites produced from the amino groups. Two implications of such a surface modification are to adhesion and blood compatible materials preparation.

INTRODUCTION

A large amount of interest has developed recently in the study of reactions or interactions of low temperature gaseous plasmas with solid substrates. This interest has been partly motivated by aerospace research and partly by the materials sciences. Of particular interest is the manner in which low temperature gaseous plasmas consisting of atoms, free radicals, and excited states, both ionic and neutral, behave at the surface of polymeric materials. Such interactions as an oxygen or helium plasma with polyethylene, Teflon, and a variety of other polymers have produced useful end results in terms of improved adhesion¹ or induced wettability.²

Surface interactions with plasmas usually fall into three general classes of reaction possibilities: (1) units in the polymer can be abstracted from the surface, (2) entities can be added to the surface from the discharge, or (3) rearrangement of bonds can occur within the surface of the polymer

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itself. It is possible that more than one of the above reaction classes will occur concomitantly.

The nature of plasma reactions with polymer surfaces is quite different from those reactions induced by ionizing, γ -, or β -irradiation procedures. These latter techniques usually penetrate deep into the bulk of the polymer grossly affecting the bulk characteristics. Low-temperature plasma interactions even at long exposure times affect materials only over a range of hundreds to several thousand angstroms in depth. For example, exposure of polyethylene to activated helium (100 W) for 15 min caused unsaturation and crosslinking to occur to a depth of about 5000 Å into the surface region.^{3,4} Thus, plasmas can be regarded as a very soft radiation source. Another prime difference between plasmas and alternate surface modification techniques is the greater chemical flexibility one can realize in terms of the choice of reactant gas or mixtures for producing reactive species to produce various surface states. The plasma surface modification technique is a dry gas-solid process usually free of secondary reactive species causing undesirable side effects.

In the present case, the reactions of several types of polymers with RF electrodelessly excited ammonia or 1:2 nitrogen/hydrogen mixtures are reported which suggest that amino groups are being added to the surface from species in the discharge without undue compromise of the bulk characteristics of the polymers. Such a controllable surface modification is technologically noteworthy, since surface amino pendants with their associated polarity and reactivity can relate to areas of preparation of blood compatible materials, promotion of adhesion, as well as subsequent organic reactions with the amino groups for other desirable end results. The full significance and evaluation of the gaseous plasma approach to blood compatible materials preparation and the biomedical evaluation of these materials will be described elsewhere.⁵

EXPERIMENTAL

Materials

The gases utilized in the plasma experiments and the stated purity are as follows: anhydrous ammonia (99.99% min., Matheson), nitrogen (99.997% min., Matheson), and hydrogen (99.999% min., Matheson). The gases and reagents were used without attempts to purify them any further.

The polymers investigated in this study and their sources are as follows: poly(vinyl chloride), Dayton Plastics, Cleveland, Ohio; polytetrafluoroethylene, Dayton Plastics, Cleveland, Ohio; polycarbonate, Dayton Plastics, Cleveland, Ohio; polypropylene, Cordite Corporation, Cleveland, Ohio; polyurethane (Roylar) U. S. Royal, cured at Battelle; poly(methyl methacrylate) (Korad-A), Rohm and Hass. The polymers represent candidate materials that are being considered and evaluated for artificial heart fabrication by several research teams.

Radiofrequency Equipment and Run Procedure

The plasmas were established by electrodeless excitation at radiofrequencies.⁶ A crystal-controlled frequency of 13.56 MHz was employed for all the experiments. The experimental requirements and the nature of the radiofrequency excitation equipment employed in this study have been discussed elsewhere.^{7,8} The apparatus employed is depicted in Figure 1. In the experiments involving plasmas, nondissociated gases were passed at 0.30 to 1.5 torr into a manifold of discharge tubes passing between external capacitive excitation plates. Gas excitation took place at 50–500 W of net RF power delivered from the radiofrequency generator (RFG-1500, Tracerlab, a Division of LFE, Inc.). Power was measured by a radiofrequency wattmeter capable of reading forward and reflected power. The difference in readings provided the net power going into the discharge. The particular matching network employed permitted efficient matching of the output impedance of the generator (50 ohm) to that characteristic of the partially ionized gas load.⁷ Once ionized and dissociated, the plasma passed into the 2.3 liter reactor and encountered the five polymer samples lying as 2-in. diameter circular films 1–5 mils thick on a glass support within the reactor. After reaction at the sample surface, the flowing gas quickly deactivated and passed out the exhaust system as neutral gases along with any product gases. Temperatures established at the sample surface were measured remotely by means of infrared radiation pyrometry.⁷

The run procedure consisted of placing the polymer samples on a glass tray which slipped into the plasma reactor in such a fashion that the five samples were positioned directly below each of the five inlet tubes of the

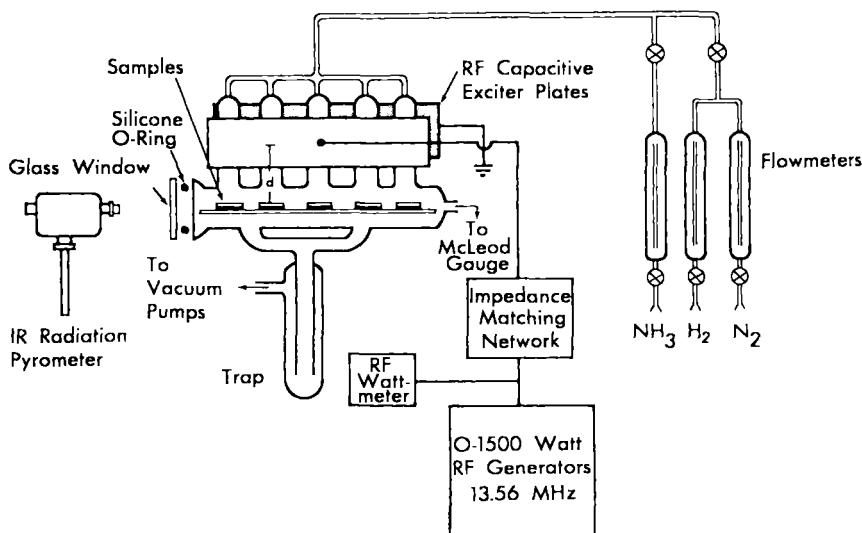


Fig. 1. Capacitive flow discharge apparatus with accompanying RF, temperature, and gas regulation assemblies.

plasma reactor. So arranged, each sample encountered identical plasma conditions, geometry, ambient temperature, etc. The pressure of the system was reduced to $<10 \mu$ before admitting the desired ammonia or nitrogen/hydrogen gas mixture at the desired flow rate commensurate with the ultimate system pressure to be established. After purging the system for 10–15 min, the power from the RF generator was slowly increased, until the gas discharge was initiated. Efficient coupling of the RF energy to the gas load was immediately achieved by proper adjustment of the inductive "L" and capacitive "C" controls on the matching network. Physically, the correct matching was observed by reducing the reflected power, as read on the RF wattmeter, to a minimum value, usually 0.5–1.0 W in the 200-W range or 4–10 W in the 800-W range.

Once established, the plasma conditions were quite stable, so long as gas flow conditions remained constant, throughout the course of the experiment. The gaseous plasma parameters that were varied in the experiments reported here were system pressures and residence times. Pressures were varied from 0.3 to 1.5 torr, while residence times varied from three to fourteen hours. As a first step in the parameterization of the system, the upper limit of power level P_{\max} was established at which the polymers began to show any visible signs of deformation or other physical compromise. These are reported in Table I for specimens lying perpendicular to the flow discharge tubes approximately 6 in. from the midpoint of the capacitive exciter plates, (d), in Figure 1.

TABLE I

Polymer	P_{\max} , W
Poly(vinyl chloride)	550
Polytetrafluoroethylene	>1000
Polycarbonate	800
Polypropylene	250
Polyurethane	200
Poly(methyl methacrylate)	100

Ultimately for any processing requirements, the temperature/power restrictions can be relaxed by the use of cooled processing substrates acting as a heat sink on which the polymers rest or contact.

Surface Characterization

Once the amino sites were formed at the polymer surface via the gaseous plasma technique, they were then amenable to a subsequent alkylation reaction in solution to form quaternary ammonium sites. The alkylation of the amino sites on the films was accomplished by immersing the films for 24 hr in a 10% solution of methyl iodide in methyl alcohol.⁹ The quaternary sites were then capable of forming stable complexes with the negatively charged sulfate ester groups of heparin, a blood ant clotting agent. Control samples with no plasma treatment showed negligible reactivity toward the alkylating agent.

The procedures for heparinization have been described by Falb et al. in other reports.⁹ The complex which results is ionic in nature, and its stability is dependent ultimately on the structure of the quaternary salt.¹⁰ In this study no variation in the quaternary structure is possible, since it is presumed that only primary amino sites are developing on the polymer surfaces during the discharge or plasma phase of the surface treatment. Other gaseous plasma reactants might well lead to more optimum amino structures with different bonding constants toward heparin and thus improved stability.

In order to measure more quantitatively the degree of heparin attachment to the quaternary sites, the use of a heparin derivative tagged with ³⁵S was employed.¹⁰ In this manner the uptake of the heparin could be followed by the ³⁵S activity. Counting was performed by a 2 π low beta counter. Since the geometry of the samples was known (ca. 2-in. diameter flat films) as well as the original concentration of the radioactive heparin solution, the calculation was made in which an effective heparin "thickness" (in Angstroms) bound to the surface could be derived. This value is expressed in subsequent tables in reference to the various polymers. The degree of heparin attachment, reported as thicknesses, is proportional to the original amino site density.

RESULTS AND DISCUSSION

Nature of the Plasma

Ammonia or nitrogen/hydrogen mixtures under conditions of the electrodeless discharge represent a fairly complex system of neutral, ionic, free-radical, and atomic species. Such species as N, H, NH, and NH₂ are generally accepted as neutral reactive intermediates in discharge,¹¹ radiolysis,¹² and photolysis¹³ experiments with ammonia in nearly the same ranges of energetic electron abundance or gas pressure. In certain of the latter experiments, both positive and negative ions of the neutral intermediates are proposed.

The plasma diagnostics for nitrogen-hydrogen mixtures have never been studied in any great detail. The nature of such gas compositions has, however, been studied in terms of hydrazine synthesis, for example, where final products or degrees of conversions were investigated, but no attempt has been made to unravel quantitatively the existence and concentration of reactive intermediates. However, the results of this study indicate a sufficient similarity exists between NH₃ and N₂/H₂ plasmas to justify invoking the same reactive intermediates in the gas phase towards the ultimate formation of amino groups at the surface.

Behavior of the Various Polymers in Plasmas

Polypropylene. Polypropylene showed heparin attachment thicknesses as seen in Table II. No pretreatment of the polymer was performed except for a toluene rinse, where indicated, prior to the plasma treatment.

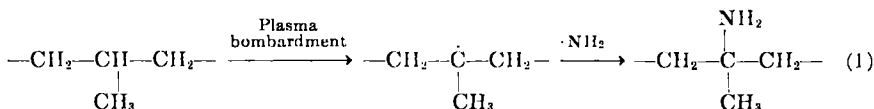
TABLE II
 Plasma Reactions with Polypropylene

Gas type ^a	Power, W	Exposure time, min	Pressure, torr	Surface temp T, °C	Heparin bound, Å
A	200	180	0.3	95	39
A	150	840	0.3	95	44
A	100	180	0.3	34	50
B	200	180	0.3	94	30
B	200	480	0.3	102	124
B ^b	100	180	0.3	35	40
B	75	720	1.0	70	43

^a Gas type: A = NH₃; B = N₂:2H₂.

^b Toluene wash prior to plasma treatment.

Two significant results emerge: (1) with N₂:2H₂ (a ratio chosen empirically for the reaction N₂ + 2H₂ → 2NH₃) the attachment of amino groups is enhanced at lower pressures and longer times at higher RF powers; (2) the use of NH₃ appears to give a degree of -NH₂ attachment independent of power and time variation. Longer exposure at high powers may optimize attachment. If results of studies of uv-irradiation of polypropylene¹⁴ can be extended to reactive surface irradiation with plasmas, then radicals and reaction as in eq. (1) are probably occurring at the surface.



Attempts to follow the reaction via FMIR (frustrated multiple internal reflectance) techniques failed in that no bands attributable to N-H stretching or -NH₂ deformation could be seen. This is no doubt due to modest coverage on the surface outside the limits of detection by FMIR. For several polymer films investigated in this study poor film contact is also suspected as a cause for inability to detect amino absorption bands.

Poly(vinyl chloride) (PVC). Both CaCO₃ filled and unfilled PVC were examined. The data in Table III reflect that fairly significant attachment can be achieved employing both plasmas of NH₃ and N₂:2H₂ composition for filled polymers. It is also apparent that with either plasma composition at approximately 100–150 W, 360 min, and pressures ranging from 0.3 to 1.5 torr, maximum thicknesses are being achieved. In experiments employing either NH₃ or N₂:2H₂ plasmas at very long residence times, 720 min, very low thicknesses of bound heparin were achieved. This perhaps reflects rupture and fragmentation of the surface molecular structure due to continued plasma bombardment and ablative effects. Unfilled polymers were studied at lower powers since they were thermally less stable than filled polymers, i.e., began melting at RF powers approaching 150 W.

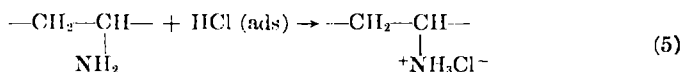
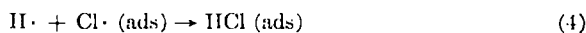
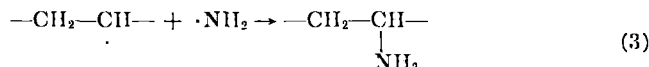
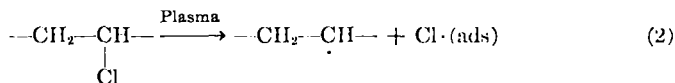
The reaction taking place at the surface of the polymer may very well

TABLE III
 Plasma Reactions with Polyvinylchloride

Gas type ^a	Power, W	Exposure time, min	Pressure, torr	Surface temp, T, °C	Heparin bound, Å
Filled Polymers					
A	150	180	0.3	90	111
A	150	360	0.3	80	135
A	150	180	1.0	55	143
A	150	360	1.0	50	159
A	150	720	1.0	75	32
B	150	360	1.0	110	182
B	150	720	1.0	75	27
C	100	360	1.5	40	70
Unfilled polymer*					
A	75	180	0.3	30	42
B	75	180	0.3	31	32
A	100	360	1.5	31	90

^a Gas type: A = NH₃; B = N₂:2H₂; C = N₂ : 3H₂

be that of salt formation due to chemisorbed HCl formed from hydrogen and chlorine atoms [eqs. (2)–(3)].



FMIR spectra show an intense absorption occurring at 3137 and 3040 cm⁻¹, indicative of NH₄⁺ type structures. Good surface contact in the FMIR cell was achieved with PVC samples.

Polyurethane. Polyurethane as received and as pretreated with a hot methanolic rinse was exposed to varying conditions of plasmas. The discharge conditions which gave the maximum thickness of heparin occurred with N₂:2H₂ plasmas and are summarized in Table IV.

Other samples treated at longer times (720 min) and lower pressures gave thicknesses on the order of 15 Å, perhaps due to similar ablative effects observed in PVC.

Polycarbonate (PC) and Poly(methyl Methacrylate) (PMM). The data in Table V helps to confirm that better amino attachment is obtained more generally with N₂:2H₂ plasmas rather than with pure ammonia. It is inconclusive at this moment whether time or pressure at given power levels have the greatest influence on amino attachment.

One might predict that -NH₂ insertion into the surfaces of PC and PMM

TABLE IV
 Plasma Reactions with Polyurethane^a

Gas type ^b	Power, W	Exposure time, min	Pressure, torr	Surface temp T, °C	Heparin bound, Å
A	150	720	1.0	<60	46
A	150	360	1.0	42	35
A	100	180	1.5	32	62
B	150	360	1.0	36	33
B	100	180	1.5	34	101

^a All polymers methanol-rinsed.

^b Gas type: A = NH₃; B = N₂:2H₂.

 TABLE V
 Plasma Reactions with PC and PMM

Polymer	Gas type ^a	Pre-treatment ^b	Power, W	Exposure time, min	Pressure, torr	Surface temp T, °C	Heparin bound, Å
Polycarbonate	B	a	400	360	0.3	85	56
	A	b	200	180	1.5	42	38
	A	b	400	360	0.3	85	42
	B	b	200	180	1.5	40	90
Poly(methyl methacrylate)	B	b	75	720	0.3	30	48
	A	b	75	180	1.5	30	14
	B	b	75	180	1.5	29	29
	A	c	75	720	0.3	29	89

^a Gas type: A = NH₃; B = N₂:2H₂.

^b Pretreatment: a = no pretreatment; b = methanol rinse; c = 2-propanol rinse.

would follow analogous pathways for alternate methods of introducing these groups by solution techniques^{9,10} or from predictions as to radical recombination sites developing in the polymer surface after γ -irradiation.¹⁵ The exact structural details for -NH₂ groups residing in these polymers is not known at present and would require further kinetic investigation.

Polytetrafluoroethylene (PTFE). With PTFE, unsaturation sites are doubtlessly developing at the surface due to plasma bombardment,¹ along with amino sites. Coverages with heparin appear modest with most of the discharge conditions employed. As Table VI indicates, there is no pronounced difference between NH₃ and N₂:2H₂ plasmas to add amino groups, although there is some modest indication that NH₃ may be slightly more effective.

No FMIR detection of -NH₂ groups was observed. The mechanism of -NH₂ groups entering the surface would invoke plasma bombardment forming -CF₂-CF- surface radicals which subsequently combine with ·NH₂ radicals in the plasma.

TABLE VI
Plasma Reactions with Polytetrafluoroethylene^a

Gas type ^b	Power, W	Exposure time, min	Pressure, torr	Surface temp T, °C	Heparin bound, Å
A	200	180	0.3	29	46
A ^c	250	360	0.3	45	60
B	200	180	0.3	30	39
B ^c	250	360	0.3	45	53

^b Gas type: A = NH₃; B = N₂:2H₂.

^a 1:1 Toluene/acetone pre-rinse in all cases.

^c Reduction of surface by 2% sodium hydrosulfite-5% NaHCO₃ prior to quaternization.

CONCLUSIONS

Results from this study demonstrate that amino groups generated in low temperature, gaseous plasmas can be introduced into the surface structure of several types of polymers. This surface modification via a dry gas-solid reaction approach provides definite advantages for certain end uses of these polymers. One may desire to add functionality to a surface which is not in contact with a chemically reacting solution containing many secondary species. These species can permeate into the surface region of the polymer resulting in undesirable chemical or mechanical effects relating to adhesion, biomedical factors, or other problems where the question of the interface or good interfacial contact is significant.

Although the data derived in this study indicate that amino groups are being added to the surface, there is still the requirement in some instances that even greater amounts of amino sites be developed. In every case the plasma treatment led to heparin binding which retarded the coagulation of blood, but did not prevent it. Thus the full optimization of plasma discharge conditions—power, pressure, residence time as well as the composition of the starting gas—requires further refinement, and presumably would have to be studied with respect to each individual polymer.

It appears also that the low-temperature plasma approach should offer a great amount of potential to add other than amino groups to surfaces depending on the nature of reactive intermediates existing within the plasma. To date studies with plasmas interacting with polymer surfaces have been largely concerned with oxidative or crosslinking processes. Experiments with other nitrogen-containing gases, as well as sulfur, halogen, or alkyl plasmas¹⁶ should provide profitable research avenues.

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